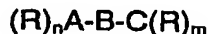


1. A process for the oligomerisation of olefins which includes the step of contacting an olefinic feedstream with a catalyst system which includes the combination of:

- a transition metal compound; and
- a heteroatomic ligand described by the following general formula



where

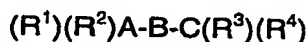
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different and each R is independently selected from a homo hydrocarbyl group and a heterohydrocarbyl group, and at least one R is substituted with a polar substituent; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

each of R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group;

at least one of R^1 , R^2 , R^3 and R^4 , if aromatic is substituted with a polar substituent on a 2nd or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 , if they are aromatic, are not on the atom adjacent to the atom bound to A or C.

2. The process as claimed in claim 1 wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth, and nitrogen; B is a linking group between A and C; and each of R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group.
3. The process as claimed in claim 2, wherein up to four of R^1 , R^2 , R^3 and R^4 have substituents on the atom adjacent to the atom bound to A or C.
4. The process as claimed in claim 2 which is a tetramerisation process and wherein each of R^1 , R^2 , R^3 and R^4 is aromatic, including heteroaromatic, but not all of R^1 , R^2 , R^3 and R^4 are substituted by a substituent on an atom adjacent to the atom bound to A or C.
5. The process as claimed in claim 4, wherein not more than two of R^1 , R^2 , R^3 and R^4 have substituents on the atom adjacent to the atom bound to A or C.
6. The process as claimed in any one of claims 2 to 5, wherein each polar substituent on one or more of R^1 , R^2 , R^3 and R^4 is electron donating.
7. The process as claimed in either one of claims 4 or 5 wherein the feedstream includes an α -olefin and the product stream includes at least 30% of a tetramerised α -olefin monomer.
8. The process as claimed in claim 7 wherein the olefinic feedstream includes ethylene and the product stream includes at least 30% 1-octene.
9. The process as claimed in any one of claims 1 to 8 wherein the olefinic feedstream includes ethylene and wherein the $(C_6 + C_8) : (C_4 + C_{10})$ ratio in the product stream is more than 2.5:1.
10. The process as claimed in either one of claims 1 or 4, wherein the olefinic feedstream includes ethylene and wherein the $C_8 : C_6$ ratio in the product stream is more than 1.

11. The process as claimed in any one of claims 1 to 10 wherein the pressure is greater than 100 kPa (1 barg).
12. The process as claimed in any one of claims 8 to 10 wherein ethylene is contacted with the catalyst system at a pressure of more than 1000 kPa (10 barg).
13. The process as claimed in any one of claims 1 to 12 wherein A and/or C are a potential electron donor for coordination with the transition metal.
14. The process as claimed in any one of claims 1 to 13 wherein B is selected from the group consisting of an organic linking group comprising a hydrocarbyl, a substituted hydrocarbyl, a hetero hydrocarbyl or a substituted hetero hydrocarbyl; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.
15. The process as claimed in claim 14 wherein B is a single atom linking spacer.
16. The process as claimed in claim 14 wherein B is $-N(R^5)-$, wherein R^5 is selected from the groups consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.
17. The process as claimed in any one of claims 1 to 16, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
18. The process as claimed in any one of claims 1 to 16, wherein A and C is independently phosphorous or phosphorous oxidised by S or Se or N or O.
19. The process as claimed in claim 2 wherein R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl,

thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.

20. The process as claimed in claim 1 or claim 2 wherein the ligand is selected from the group consisting of (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)₂PN(isopropyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-ethylhexyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂, (3-methoxyphenyl)(phenyl)PN(methyl)P(3-methoxyphenyl)(phenyl), (4-methoxyphenyl)(phenyl)PN(methyl)P(4-methoxyphenyl)(phenyl), (3-methoxyphenyl)₂PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)₂PN(methyl)P(phenyl)₂, (4-methoxyphenyl)₂PN(1-cyclohexylethyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-methylcyclohexyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(decyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(pentyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(benzyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(phenyl)P(4-methoxyphenyl)₂, (4-fluorophenyl)₂PN(methyl)P(4-fluorophenyl)₂, (2-fluorophenyl)₂PN(methyl)P(2-fluorophenyl)₂, (4-dimethylamino-phenyl)₂PN(methyl)P(4-dimethylamino-phenyl)₂, (4-methoxyphenyl)₂PN(allyl)P(4-methoxyphenyl)₂, (4-(4-methoxyphenyl)-phenyl)₂PN(isopropyl)P(4-(4-methoxyphenyl)-phenyl)₂ and (4-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂.

21. The process as claimed in any one of claims 1 to 20 wherein the catalyst system is prepared by combining in any order the heteroatomic ligand with the transition metal compound and an activator.

22. The process as claimed in claim 21, which includes the step of adding a pre-formed coordination complex, prepared using the heteroatomic ligand and the transition metal compound, to a reaction mixture containing the activator.

23. The process as claimed in claim 21, which includes the step of generating a heteroatomic coordination complex *in situ* from the transition metal compound and a heteroatomic ligand.

24. The process as claimed in any one of the claims 1 to 23, wherein the transition metal in the transition metal compound is selected from the group

consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.

25. The process as claimed in claim 24, wherein the transition metal is chromium.

26. The process as claimed in any one of claims 1 to 25, wherein the transition metal compound is selected from the group consisting of an inorganic salt, an organic salt, a co-ordination complex and an organometallic complex.

27. The process as claimed in claim 26 wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.

28. The process as claimed in claim 27, wherein the transition metal compound is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.

29. The process as claimed in any one of claims 1 to 28, wherein the transition metal from the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.01:100 to 10 000:1.

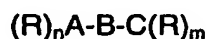
30. The process as claimed in any one of claims 21 to 23 wherein the catalyst system includes an activator selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, such as methyl lithium and methylmagnesium bromide, an inorganic acid and salt, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

31. The process as claimed in claim 30, wherein the activator is an alkylaluminumoxane.

32. The process as claimed in claim 31, wherein the transition metal compound and the aluminumoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 10 000:1.

33. A tetramerisation catalyst system which includes the combination of:

- a transition metal compound; and
- a heteroatomic ligand described by the following general formula



where

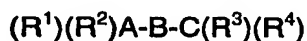
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different and each R is independently selected from a homo hydrocarbyl group and a heterohydrocarbyl group, and at least one R is substituted with a polar substituent; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

each of R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group;

at least one of R^1 , R^2 , R^3 and R^4 , if aromatic is substituted with a polar substituent on a 2nd or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 , if they are aromatic, are not on the atom adjacent to the atom bound to A or C.

34. The catalyst system as claimed in claim 33 wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from the group consisting of phosphorus, arsenic, antimony,

bismuth, and nitrogen; B is a linking group between A and C; and each of R¹, R², R³ and R⁴ is independently selected from the group consisting of a non-aromatic group, an aromatic group, and a heteroaromatic group.

35. The catalyst system as claimed in claim 34 wherein each of R¹, R², R³ and R⁴ is aromatic, including heteroaromatic, but not all of R¹, R², R³ and R⁴ are substituted by an substituent on an atom adjacent to the atom bound to A or C.

36. The catalyst system as claimed in claim 35, wherein not more than two of R¹, R², R³ and R⁴ have substituents on the atom adjacent to the atom bound to A or C.

37. The catalyst system as claimed in any one of claims 34 to 36, wherein each polar substituent on one or more of R¹, R², R³ and R⁴ is electron donating.

38. The catalyst system as claimed in any one of claims 33 to 37, wherein A and/or C are a potential electron donor for coordination with the transition metal.

39. The catalyst system as claimed in any one of claims 33 to 38, wherein B is selected from the group consisting of an organic linking group comprising a hydrocarbyl, a substituted hydrocarbyl, a hetero hydrocarbyl and a substituted hetero hydrocarbyl; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, -B(R⁵)-, -Si(R⁵)₂-, -P(R⁵)- and -N(R⁵)- where R⁵ is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.

40. The catalyst system as claimed in claim 39, wherein B is a single atom linking spacer.

41. The catalyst system as claimed in claim 39, wherein B is selected to be -N(R⁵)-, wherein R⁵ is selected from the groups consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.

42. The catalyst system as claimed in any one of claims 33 to 41, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.

43. The catalyst system as claimed in any one of claims 33 to 41, wherein A and C is independently phosphorus or phosphorus oxidised by S or Se or N or O.

44. The catalyst system as claimed in any one of claims 1 to 43 wherein the ligand is selected from the group consisting of (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)₂PN(isopropyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-ethylhexyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂, (3-methoxyphenyl)(phenyl)PN(methyl)P(3-methoxyphenyl)(phenyl), (4-methoxyphenyl)(phenyl)PN(methyl)P(4-methoxyphenyl)(phenyl), (3-methoxyphenyl)₂PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)₂PN(methyl)P(phenyl)₂, (4-methoxyphenyl)₂PN(1-cyclohexylethyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-methylcyclohexyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(decyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(pentyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(benzyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(phenyl)P(4-methoxyphenyl)₂, (4-fluorophenyl)₂PN(methyl)P(4-fluorophenyl)₂, (2-fluorophenyl)₂PN(methyl)P(2-fluorophenyl)₂, (4-dimethylamino-phenyl)₂PN(methyl)P(4-dimethylamino-phenyl)₂, (4-methoxyphenyl)₂PN(allyl)P(4-methoxyphenyl)₂, (4-(4-methoxyphenyl)-phenyl)₂PN(isopropyl)P(4-(4-methoxyphenyl)-phenyl)₂ and (4-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂.

45. The catalyst system as claimed any one of the claims 33 to 44, wherein the transition metal in the transition metal compound is selected from the group consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.

46. The catalyst system as claimed in claim 45, wherein the transition metal is chromium.

47. The catalyst system as claimed in any one of claims 33 to 46, wherein the transition metal compound is selected from the group consisting of an inorganic salt, an organic salt, a co-ordination complex and an organometallic complex.

48. The catalyst system as claimed in claim 47, wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl, and chromium (III) 2-ethylhexanoate.

49. The catalyst system as claimed in of claim 48, wherein the transition metal is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.

50. The catalyst system as claimed in any one of claims 33 to 49, wherein the transition metal from the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand ratio from about 0.01:100 to 10 000:1.

51. The catalyst system as claimed in any one of claims 33 to 50, which includes an activator.

52. The catalyst system as claimed in claim 51, wherein the activator is selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, such as methyllithium and methylmagnesium bromide, an inorganic acid and salt, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

53. The catalyst system as claimed in claim 52, wherein the activator is an alkylaluminoxane.

54. The catalyst system as claimed in claim 53, wherein the alkylaluminoxane is selected from the group consisting of methylaluminoxane (MAO), ethylaluminoxane (EAO) modified alkylaluminoxanes (MMAO), and mixtures thereof.

55. The catalyst system as claimed in claim 53 or claim 54, wherein the transition metal and the aluminoxane are combined in proportions to provide an Al/transition metal ratio from about 1:1 to 10 000:1.

56. Use of a catalyst system as claimed in any one of claims 33 to 55 for the tetramerisation of olefins.

57. Use of a catalyst system as claimed in any one of claims 33 to 55 for the tetramerisation of ethylene.